THE STRUCTURAL AND OPTICAL PROPERTIES OF HYDROGENATED AMORPHOUS CARBON (a-C:H) THIN FILMS DEPOSITED USING A DIRECT CURRENT-PLASMA ENHANCED CHEMICAL VAPOUR DEPOSITION (DC-PECVD) TECHNIQUE

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ABSTRACT

Hydrogenated amorphous carbon (a-C:H) thin films were deposited using the DC plasma enhanced chemical vapour deposition (DC-PECVD) technique. The effects of the deposition parameters (chamber pressure, electrode distance, CH_4 flow rate, and substrate temperature) on the deposition rate were studied. It was found that with increasing DC power, *w* and hence ion bombardment energy, *E* the deposition rate increased initially and then decreased after passing a maximum. The increase in deposition rate of the a-C:H films with increasing ion energy is explained by the increase in the concentration of dangling bond sites on the growing film surface. Further analyses which were based on the films, revealed the optimum deposition rate for every set of deposition parameters. Both power and ion bombardment energy were continuously changing during the deposition, as a results of varying deposition parameters. The films properties ranged from polymer-like (PAC) to graphite-like (GAC) a-C:H films, as the power and ion energy increased. In order to study the structure and the optical properties of a-C:H films, infrared and Raman spectroscopy, XRD, SEM, Ellipsometer, UV-Vis Spectrophotometer and photoluminescence, were used as characterization techniques to extract information on sp^3/sp^2 and hydrogen contents, amorphous nature, morphology, optical gap, E_0, absorption coefficient, α, photoluminescence response, refractive index, *n*, and extinction coefficient, *k*, of the a-C:H films. Based on these results, the films studied in the present research are found to consist of sp^2 clusters of which their size increases with increasing power and ion bombardment energy during the deposition, resulting in lower hydrogen, sp^3 content and optical gap. This confirms the model proposed by Robertson where sp^2 content controls the optical gap. The increase in hydrogen freed from the films at higher ion energies results in an increase in the sp^2 fraction, bigger cluster size and graphitic structures of the films.

ABSTRAK

Filem tipis amorfus karbon terhidrogen telah disediakan menggunakan teknik pemendapan wap kimia yang diperkuat plasma, yang menggunakan arus terus (DC-PECVD). Kesan parameter pemendapan (tekanan kebuk, jarak elektrod, kadar alir CH_4 dan suhu substrat) terhadap kadar pemendapan telah dikaji. Di dapati dengan bertambahnya kuasa, *w* dan kemudiannya tenaga hentaman ion, *E* kadar pemendapan bertambah pada awalnya dan kemudian berkurang setelah mencapai satu nilai maksimum. Pertambahan di dalam kadar pemendapan filem a-C:H dengan bertambahnya tenaga ion diterangkan oleh pertambahan kandungan ikatan berjuntai di atas permukaan filem yang ditumbuhkan. Analisis selanjutnya adalah berdasarkan filem yang menunjukkan kadar pemendapan yang optimum bagi setiap set parameter pemendapan. Kuasa dan tenaga hentaman ion sewaktu pemendapan adalah berubah-ubah, hasil daripada berubahnya parameter pemendapan. Filem ini mempunyai sifat antara serupa-polimer (PAC) ke serupa-grafit (GAC) filem a-C:H, apabila kuasa dan tenaga ion bertambah. Untuk mengkaji sifat struktur dan optik bagi filem a-C:H, spektroskopi inframerah dan Raman, XRD, SEM, Ellipsometer, UV-Vis Spektrofotometer dan fotoluminesen, telah digunakan sebagai teknik pencirian untuk mendapatkan maklumat mengenai sp^3/sp^2 dan kandungan hidrogen, sifat amorfus, morfologi, jurang optik, E_0, pekali penyerapan, α, tindakbalas fotoluminesen, indeks biasan, *n*, dan pekali penghapusan, *k* bagi filem a-C:H. Berdasarkan keputusan, filem yang dikaji dalam penyelidikan ini, mengandungi kluster sp^2 yang mana saiznya meningkat dengan meningkatnya kuasa dan tenaga hentaman ion sewaktu pemendapan, lalu menyebabkan kandungan hydrogen, sp^3 dan jurang optik berkurang. Ini mengesahkan model yang dicadangkan oleh Robertson di mana kandungan sp^2 mengawal jurang optik. Peningkatan pembebasan hidrogen daripada filem pada tenaga ion yang lebih tinggi menyebabkan terhasilnya pertambahan di dalam pecahan sp^2, saiz kluster yang lebih besar dan filem berstruktur grafit.

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LIST OF SYMBOLS

E_0	-	optical band gap
α	-	absorption coefficient
E_g	-	energy band gap
β	-	Huckel parameter
C	-	carbon
D	-	disorder
G	-	graphite
I_D	-	disorder intensity
I_G	-	graphite intensity
λ	-	wavelength
λ_{mfp}	-	mean free path
k	-	extinction coefficient
E_{em}	-	emission band
E_{PL}	-	PL peak energy
I_T	-	transmission intensity
I_A	-	absorption intensity
I_R	-	reflection intensity
I_o	-	impinging light intensity
I_T/I_o	-	transmissivity
I_R/I_o	-	reflectivity
I_A/I_o	-	absorptivity
E	-	ion bombardment energy
h	-	Planck constant
c	-	light velocity
$h\nu$	-	photon energy
n	-	refractive index
n^*	-	complex refractive index

R	-	reflection
V_c	-	cathode potential
V_p	-	plasma potential
ν_o	-	frequency of light
$h\nu_R$	-	scattering energy
$h\nu_o$	-	incident photon
$h\nu_s$	-	scattered photon
Δ	-	phase difference
ψ	-	arc tangent factor
$A_1^{'}$	-	first analyzer reading
$A_2^{'}$	-	second analyzer reading
P_1	-	first polarizer reading
P_2	-	second polarizer reading
FWHM	-	full width half maximum
R_d	-	deposition rate
Φ	-	ion flux
m	-	mass
ρ	-	density
S	-	sticking coefficient
τ	-	adsorption time
k	-	Boltzmann constant, 1.38066×10^{-23} JK^{-1}
T	-	temperature
w	-	power
L	-	sheath thickness
p	-	pressure
σ	-	collision cross-section

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CHAPTER I

INTRODUCTION

1.1 Introduction

Thin films are solid materials of either metal, semiconductor or insulator, deposited onto substrates at film thickness in the range of 10 to1000 nm (Chopra, 1969). Beyond this range they are refered to as thick films. While the term ultra thin film refers to the latest science frontier in which the film thickness is much thinner than100 nm. Its thickness creates different characteristics compare to the original bulk material and this contributes to a few new phenomena. Substrate is a kind of solid that can support the formation of thin film on it. It is usually a material that does not chemically interact with the film. A clean and smooth surface of substrate is required in order to obtain good quality and homogeneous films. Nowadays, we can see thin films widely used in electronics, optoelectronic devices and other optical and surface engineering applications (Kazmerski, 1980).

Thin films can be produced by utilizing several methods. Generally, the preparation of thin films can be classified into 2 methods; physical and chemical techniques (Abu Talib *et al.*, 1993). Some examples of physical vapour deposition are vacuum evaporation and sputtering. There is also variety in the chemical vapour deposition processes such as plasma enhanced (assisted) chemical vapour deposition (PECVD, PACVD), low-pressure chemical vapour deposition (LPCVD), etc. Thin film product can be either in the form of single crystal, polycrystalline or amorphous, this depends on several deposition factors such as temperature, pressure and etc.

1.2 Research Background

The past 25 years have seen an increase in the level of interest in the deposition and characterization of hydrogenated amorphous carbon (a-C:H) thin films due to its novel optical, mechanical and electrical properties of these films and its similarities to diamond (Grill, 1999, Dachuan *et al.*, 1996 and Robertson, 2002). The main properties of diamond are low optical absorption throughout the UV, visible and IR regions, high electrical resistivity, high thermal conductivity, chemical resistance to most acids and solvent, hardness and low coefficient of friction (May, 1995, 2000 and Smith, 2001). The matchless properties of natural and high-pressured synthetic diamond crystals make this material suitable for mechanical applications such as cutting and grinding, electronic applications such as high power and high frequency transistor and optical applications such as IR windows (May, 2000).

Although these applications have a very large market, they are limited by the fact that the natural diamond was only available in the form of stone or grit and for the synthetic diamond because of the small size and high cost of producing single crystalline diamond (Sagnes, 1998, May, 2000 and Smith, 2001). The production of diamond coating is now possible by chemical vapour deposition (based on low pressure vapour-phase synthesis on a substrate heated at high-temperature) and the material is often referred to as CVD diamond (Deryagin *et al.*, 1968 and Angus *et al.*, 1968). This development reduces slightly the cost and the limitation on the size of diamond, but the CVD diamond coating are polycrystalline, as opposed to natural and high-pressures synthetic diamond crystals which are normally single crystals. This polycrystalline characteristic is a drawback mainly because optical applications require smooth coatings. This is also true for electronic applications since they also require single crystal diamond. Although a number of groups have been working on producing single crystal diamond by CVD techniques, this goal has not yet been achieved (Sagnes, 1998 and May 2000).

An alternative form of carbon coating is now becoming available. It is known as hydrogenated amorphous carbon (a-C:H) thin films, one of the diamond-like carbon (DLC) form . Aisernberg and Chabot, (1971) were the first to produced

diamond-like carbon by ion beam deposition techniques. The name diamond-like carbon came originally from the unrecognizable diffraction pattern obtained on the samples. It is however, generally accepted that this term means hard and structurally amorphous. Hydrocarbon gases were applied in the deposition process; therefore not only carbon was incorporated in the growing films but also hydrogen. Angus *et al.* (1986) defined pure DLC composed of carbon and/or hydrogen into two categories; hydrogenated amorphous carbon (a-C:H) and amorphous carbon, (a-C). The first type contains from less than 10% to 60% hydrogen; incorporations of hydrogen in this type of DLC are important for obtaining diamond-like properties. The second type, amorphous carbon contains less than 1% hydrogen. This material is not a good electrical, optical or mechanical material compared to a single crystal diamond, but it is satisfactory for many applications such as a protective coating in areas such as optical window, scratch resistant, magnetic storage disk, biomedical coating, and low friction wear resistant coatings for moving part in tools (Manage, 1998 and Robertson, 2002).

Diamond is a material with a well-defined structure and has properties that vary within a relatively narrow range of values. Meanwhile a-C:H has a structure and composition that varies considerably with deposition parameters, as a result, so does its properties (Pierson, 1993). Therefore, if one can control these properties one can tailor them to fit specific applications. For instance, a-C:H is suitable as an anti reflection layer for germanium and silicon infrared windows and lenses (Bubenzer *et al.*, 1983 and Zhang *et al.*,1994). This application takes advantage of the adjustable refractive index of a-C:H between 1.6 and 2.2 and the low optical absorption of a-C:H in the infrared spectral region.

Several deposition methods are suitable for a-C:H thin films. These deposition methods can be classified into two large families; physical vapour deposition (PVD) and plasma enhanced chemical vapour deposition (PECVD). PVD involves the sputtering of carbon atom from a solid carbon target by energetic gas species, typically argon ions (Chopra, 1969). PECVD features a chemical process, which takes place in the vapour phase very near, or at, the substrate so that a product

is deposited onto the substrate. The reaction product is activated by creating a low pressure plasma in the vapour phase.

The feature that make PECVD attractive is; deposition at low substrate temperatures, in contrast to CVD. In PECVD the high substrate temperature is overcome when an electric discharge is created in the reactant gases to produce a significant number of free radicals, which will be much more reactive at lower temperatures while maintaining a reasonable growth rate. The growth rate will depend on the form of excitation used to create the discharge, example include RF (Mutsukura *et al.*, 1992, Benmassaoud and Paynter, 1996, Rusli *et al.*, 1996, and Jing, 1999), microwave (MW) – RF PECVD (Bouree *et al.*, 1996), RF - pulse DC mode PECVD (Taube, 1998), DC saddle field glow discharge (Manage, 1998 and Sagnes 1998), DC - RF PECVD (Dachuan *et al.*, 1996 and Cheng *et al.*, 2000), electron cyclotron resonance (ECR) - MW Plasma Chemical Vapour Deposition (ECR-MPCVD) (Zhou *et al.*, 2000), microwave electron cyclotron resonance (ECR) – RF discharge PECVD (Hong *et al.*, 2000a and Hong *et al.*, 2000b) etc.

The other distinction of PECVD over CVD is expressed by the moderate chamber pressure and therefore different qualities of the produced carbon layers as results of plasma-induced ion bombardment of the film during deposition (Vossen and Kern, 1991). Other special feature of PECVD for the fabrication of amorphous carbon films is that carbon deposition is possible over large areas and onto any given substrate. Moreover, due to the relatively low temperature, PECVD is a low-cost process as well.

In the PECVD method, two types of plasma species contribute to the film growth; the radicals, (chemically active neutral species) and ions that diffuse from the plasma and drift toward the surface. The deposition and etching processes are the ones by which ions, radicals, and their reaction products are incorporated into the growing film or are re-emitted from the surface into the gas phase. Several processes, such as sub plantation of incident ions, hydrogen sputtering and chemical adsorption of free radicals are also responsible for the films deposition. The deposition

parameters strongly affected the plasma species and the ionic energies and densities at the substrate (Mutsukura *et al.*, 1992).

Other than that, this study is very important since the structure of a-C:H is very complicated as it consists of both sp^3 and sp^2 hybridized carbon. The presence of both σ and π bond in a-C:H is precisely the root of difficulties encountered in the analysis of the structure of a-C:H. Despite the fact that the large amount of research has been done on a-C:H and as a-C:H films are already used in many technological applications, much about its structure and properties is yet to be understood. To date, the most successful model is the Robertson model (Robertson, 2002). According to this model, amorphous carbon consists of sp^2 clusters, which are embedded in sp^3 bonded matrix. Hence it is the sp^2 sites that forms band edges and controls the optical properties while sp^3 sites govern mechanical properties.

This thesis will study those problems. The DC-PECVD is the chosen technique in this study to deposit a-C:H thin films. Experiments will be done with various deposition parameters of a-C:H thin films such as chamber pressure, electrode distance, CH_4 flow rate and substrate temperature. By changing the deposition parameters of a-C:H films, one can expect to obtain different deposition rate, sp^3 and sp^2 bond distributions and different structures in the films caused it involve the change in plasma power and ion bombardment energy. Hence, the change in the properties of these films can be suited to specific applications. This study will also provide additional information on the chemical bonding and structure of a-C:H.

1.3 Research Objectives

i) To grow hydrogenated amorphous carbon (a-C:H) thin films using a DC-PECVD technique with a CH_4 gas precursor,

ii) To characterize the structural properties of a-C:H thin films using infrared and Raman spectrometer, x-ray diffraction (XRD) analysis and scanning electron microscope (SEM).

iii) To characterize the optical properties of a-C:H thin films using Ellipsometer, UV-Vis spectrophotometer and photoluminescence.

1.4 Scope of Studies

The structure and chemical bonding of a-C:H thin films will be characterized using infrared and Laser Raman spectroscopy. While to confirm the presence of amorphous structures in the a-C:H thin films, it will be characterized using x-ray diffraction (XRD). Scanning electron microscopy (SEM) will be used to characterize the morphology of the a-C:H films; their uniformity, smoothness and pinhole sites. The thickness, refractive indices, *n* and extinction coefficient, *k* of the films will be measured using Ellipsometry technique. Meanwhile, optical properties such as optical band gap, E_0 and absorption coefficient; α will be obtained using UV-Vis spectrophotometer. While photoluminescence characterization will be used to observe the a-C:H's ability to exhibit strong room temperature photoluminescence.

Specifically, this thesis will cover 6 chapters; chapter 1 is an introduction, research background, objectives and scope of studies. The literature review regarding the properties of a-C: H films such as basic concept of carbon, the structural and optical properties and also its application are discussed in chapter 2. Chapter 3 describes basic theories of optics and semiconductor, standard DC glow discharge, plasma kinetics and basic step in thin film deposition. This chapter also provides the theory underlying the characterization technique used, which is infrared and Raman spectroscopy, XRD, SEM, Ellipsometer, UV-Vis spectrophotometer and photoluminescence . Chapter 4 will cover all the experimental and characterizations

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